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THERMODYNAMIC RELATIONS IN *n*-VARIABLE SYSTEMS IN JACOBIAN FORM

PART II

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Thermodynamic Relations in n-Variable Systems in Jacobian Form:

Part II, Polyphase Polycomponent Chemical Systems.

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1. Introduction: The Fundamental Jacobian.

In Part I[1] a general analytical theory of thermodynamic relations was developed and applied to a variety of physical systems. In the present paper the same general technique is applied to a variety of chemical systems.

Since it is possible to state the general methods and results in a form somewhat more suitable for the present case, a brief statement of the general procedure is necessary.

The starting point is the expression for dU, the differential of the internal energy. This may be written in the form

$$dU = TdS + F_1 d\theta_1 + F_2 d\theta_2 + \ldots F_n d\theta_n \qquad (1)$$

where the notation is the conventional one in thermodynamics. Thus T and S are, respectively, the absolute temperature and the entropy, while $F_1, \ldots F_n$ are the generalized forces applied to the system and $\theta_1, \ldots \theta_n$ are the conjugate geometric variables. Since in the present instance the term $F_1 d\theta_1$ will be $-pdV$, the hydrostatic work term, it is convenient to rewrite Eqn (1) in this form

$$\left.\begin{aligned} dU &= TdS - pdV + F_1 d\theta_1 + \ldots + F_l\, d\theta_l \\ \text{or} \quad dU &= TdS - pdV + \sum_{i=1}^{l} F_i\, d\theta_i,\ l = n - 2 \end{aligned}\right\} \qquad (2)$$

Here $l = n - 2$ is simply the number of differential terms (if any)

[1] F. H. Crawford, This Journal, vol. *78*, pp. 165-184, 1950. See also Phys. Rev. *72*, 521A, 1947, and Am. Jour. of Physics *17*, pp. 1-5, 1949.

above the number required for the simplest hydrostatic case. Finally n is the total number of degrees of freedom or the number of independent variables required to describe the status of the system completely. Consequently Eqn (2) must always be assumed reduced to the minimum number of terms compatible with the nature of the system.

As in Part I the variables occurring on the right side of Eqn (2) are the *primary* variables for the problem, with the various thermodynamic potentials such as U, the enthalpy H, Helmholtz's free energy A and Gibbs' potential, G, as *secondary* variables. In addition a number of *subsidiary* variables will be introduced as convenience dictates.

While in principle there is a wide choice of independent variable sets, for the most part it is convenient to make two restrictions:

(1) Each independent variable will be one of the $2n$ primaries.

(2) No conjugate pairs will be included in the set (i.e., if T is chosen then S must not be, etc.).

In the sequel a suitable set of independent variables $(x_1, x_2, \ldots x_n)$ will be called an x-set and unless otherwise stated will be a non-conjugate primary set. Once the x-set is decided upon, the remaining primaries constitute the dependent variables $(Y_1, Y_2, \ldots Y_n)$ or simply the Y-set.

In the selection of the non-conjugate x-set one variable alone must be taken from each differential term in Eqn (2). If the *first* variable is taken from each term (i.e., $T, p, F_1, \ldots F_l$) then these are said to be selected in *regular* order. Had $(T, p, F_1, \theta_2, F_3 \ldots)$ been selected, then T, p, F_1, F_3, etc., are selected in regular order while θ_2 is selected in *reverse* order. For reasons that will become apparent shortly, it is more convenient to have regular order determined by the order of the x-variable selected from some special term called the *key-term.* Thus if $F_2 d\theta_2$ were taken as the key-term and θ_2 taken as x_2, this selection would by definition fix regular order and the remaining T, p, F_1, F_3, etc., would be taken in reverse order.

It was shown in Part I that a certain Jacobian, the so-called *fundamental* Jacobian, J_0, could, once the x- and Y-sets were selected, be made the core of the subsequent treatment. This Jacobian is by definition simply the Jacobian of the Y's with respect to the x's, where the subscripts are in the order of the

terms of Eqn (2) from which the variables come, counting from left to right. Thus

$$J_o \equiv \frac{\partial\ (Y_1,\ Y_2,\ \ldots\ Y_n)}{\partial\ (x_1,\ x_2,\ \ldots\ x_n)} \tag{3}$$

and contains n^2 partial derivatives. Depending on the signs occurring in Eqn (2) and the precise way the x-set is chosen, we have some pairs of elements, symmetric about the main diagonal of the determinant, which are *equal*. Since these equalities are important in reducing the number of quantities in J_o which must be measured (directly or indirectly) experimentally, it is very important to be able to render the *entire* Jacobian symmetric. It becomes therefore of importance to modify J_o in such a way as to insure the symmetry for each choice of x-set. This new Jacobian (which may be identical with J_o and will always be so if all the terms of Eqn (1) are positive and the x-set is all selected in the *same* order) will be called the *symmetric* or *modified* Jacobian, J'_o, for the problem. Like J_o, it consists of a square array of n^2 partial derivatives. Since, however, it is symmetric we can by inspection write down equations expressing the equality of derivatives symmetrically placed about the main diagonal (i.e., conjugate pairs in the square array). These equalities are $n(n+1)/2$ in number and represent the independent *Maxwellian* relations or the equations for the "reciprocal effects" characteristic of the system.

To insure J'_o being symmetric and, as a matter of practical convenience, to avoid as many minus signs as possible, we proceed as follows. Since we can always choose all of the x-set, or all of the Y-set, as positive, let us agree to take the x-set positive and place any necessary minus signs in front of the conjugate Y's. It is convenient to give the steps for modifying J_o in a simpler way than those given in Part I and at the same time to apply them to a specific example. Thus given $dU = TdS - pdV + F_2 d\theta_2$: to set up J'_o. First: Select the desired x-set, say (T, V, θ_2). Second: Set up J_o, $J_o = \dfrac{\partial\ (S, p, F_2)}{\partial\ (T, V, \theta_2)}$. Third: Select a key-term. This is often TdS but may be any other *positive* term. It is selected so as to introduce as few minus signs in J_o as possible (using the sign

rules below). Let us then take TdS as the key term. This at once establishes *regular* and *reverse* order. Thus T is the *first* of the pair (T,S) from the key-term, whereas both V and θ_2 are the *second* members of their parent terms. Hence both V and θ_2 are selected in *reverse* order. Fourth: Modify J_o by the following sign rules for the Y-variables. Each Y is given either (a) the *sign* of its parent term (when the conjugate x-variable was selected in *regular* order) or (b) the *reversed* sign of its parent term (when the corresponding x was selected in *reversed* order).

Thus we have $J'_o = \dfrac{\partial\ (S,\ p,\ -F_2)}{\partial\ (T,\ V,\ \theta_2)}$, a Jacobian which is not only symmetric but has only one column of minus terms. Had we, on the other hand, taken $F_2 d\theta_2$ as the key term we should have had $\dfrac{\partial\ (-S,\ -p,\ F)}{\partial\ (T,\ V,\ \theta_2)}$, which is symmetric to be sure, but contains twice as many minus signs.

2. Restricted Systems.

In Part I the argument was carried out on the assumption that, in principle, any n of the $2n$ primaries could be taken for an x-set (the so-called unrestricted system). When, for various reasons, this is not so we have a *restricted* system and the specific restrictions must be kept clearly in mind. Thus if F_1 in Eqn (2) should be a function of T alone it could obviously never be in the same x-set with T. In general any variable which depends functionally on less than n other variables, is a variable of restricted functional dependence (a restricted variable for short). Restricted variables are usually chosen as Y-variables and thus automatically excluded from the x-set.

Although no a priori reasons exist for expecting a preponderance of one type of system over the other in nature, a casual survey of known systems renders it probable that restricted systems are much more numerous than unrestricted. Thus, systems involving surface tension, reversible cells, temperature radiation, and many dielectric and magnetic systems, as well as general chemical systems, all fall in the restricted class. It would appear

then that the general unrestricted system is the exception rather than the rule.

Returning to Eqn (2) let us select an x-set which contains no restricted variables, say, as an example $(T, V, \theta_1, \theta_2, \dots \theta_l)$. Then the same x-set would be unchanged in form, as would J'_o, even if the restriction should later be removed.

We have with $F_1 d\theta_1$ as the key-term:

$$J'_o = \frac{\partial\,(-S, -p, F_1, \dots F_l)}{\partial\,(T, V, \theta_1, \dots \theta_l)} = \begin{vmatrix} \frac{-\partial S}{\partial T} & \frac{-\partial p}{\partial T} & \frac{\partial F_1}{\partial T} & \cdots & \frac{\partial F_l}{\partial T} \\ \frac{-\partial S}{\partial V} & \frac{-\partial p}{\partial V} & \frac{\partial F_1}{\partial V} & \cdots & \frac{\partial F_l}{\partial V} \\ \frac{-\partial S}{\partial \theta_1} & \frac{-\partial p}{\partial \theta_1} & \frac{\partial F_1}{\partial \theta_1} & \cdots & \frac{\partial F_l}{\partial \theta_1} \\ , & , & , & & \\ , & , & , & & \\ \frac{-\partial S}{\partial \theta_l} & \frac{-\partial p}{\partial \theta_l} & \frac{\partial F_1}{\partial \theta_l} & \cdots & \frac{\partial F_l}{\partial \theta_l} \end{vmatrix} \quad (4)$$

(Note that had we taken TdS as the key term we should have had only two columns of plus terms.) Because of the symmetry of J'_o Maxwell's relations can be written down simply by inspection, beginning with

$$(\partial S/\partial V)_{T\theta_1 \dots \theta_l} = (\partial p/\partial T)_{V\theta_1 \dots \theta_l}.$$ If now

p should be a restricted variable depending, say, on

$$(T,\ V,\ \theta_1 \dots \theta_{l-1}),\ \text{then}\ (\partial p/\partial \theta_l)_{TV\theta_1 \dots \theta_{l-1}}$$

would of necessity vanish, as would its conjugate, and we should have two zeros occurring in J'_o. Due to the symmetry any off-diagonal zero automatically introduces another symmetrically placed, whereas zeros on the main diagonal may occur singly and have no effect on the number of Maxwell's relations. In the unlikely event that p depended on T alone we should have $(n-1)$ zeros in the second column. Since the first of these would be on the

main diagonal the remaining $(n-2)$ would be off diagonal and thus $(n-2)$ Maxwellian relations would become trivial. Consequently instead of having $n^2 - n(n-1)/2 = \frac{n(n+1)}{2}$ derivatives to determine from experimental data, we should have only

$$\frac{n(n+1)}{2} - (n-1) \text{ or } \frac{n(n-1)}{2} + 1;$$

and instead of $n(n-1)/2$ non-trivial and independent Maxwellian relations only $n(n-3)/2 + 2$.

3. Single Pure Substance of Variable Mass.

Let us now examine these systems in which the masses of the various constituents are to be regarded as variable. Before proceeding to the general case of chemical systems it is first of advantage to examine the special case of a single pure substance under hydrostatic pressure. Here Eqn (2) becomes

$$dU = TdS - pdV + \mu dm \tag{5}$$

where by definition $\mu = (\partial U/\partial m)_{S,V}$ and is the electrochemical potential or the Gibbs potential of a unit mass of the material. Forming the partial derivative of U with respect to m (T, p constant) gives us

$$\left(\frac{\partial U}{\partial m}\right)_{Tp} - T\left(\frac{\partial S}{\partial m}\right)_{Tp} + p\left(\frac{\partial V}{\partial m}\right)_{Tp} = \mu = u - Ts - pv \tag{6}$$

where u, s and v are the corresponding quantities per unit mass or the specific internal energy, entropy and volume, respectively. Since μ is defined then in such a way as to depend on specific and intensity variables only, it is independent of volumes and masses and therefore constitutes a restricted variable and we have here a simple example of a restricted system.

Although we are at liberty to choose any legitimate set of independent variables as the x-set, let us choose, say, (T, p, m). The Y-set is then (S, V, μ) and with μdm as the key term we write out J'_o.

$$J'_o = \frac{\partial(-S, V, \mu)}{\partial(T, p, m)} = \begin{vmatrix} \frac{-\partial S}{\partial T} & \frac{\partial V}{\partial T} & \frac{\partial \mu}{\partial T} \\ \frac{-\partial S}{\partial p} & \frac{\partial V}{\partial p} & \frac{\partial \mu}{\partial p} \\ \frac{-\partial S}{\partial m} & \frac{\partial V}{\partial m} & \frac{\partial \mu}{\partial m} \end{vmatrix} = \begin{vmatrix} \frac{-m\partial s}{\partial T} & \frac{m\partial v}{\partial T} & -s \\ \frac{-m\partial s}{\partial p} & \frac{m\partial v}{\partial p} & v \\ -s & v & o \end{vmatrix} \quad (7)$$

Since $\mu = \mu(T, p)$, $(\partial\mu/\partial m)_{Tp}$ must vanish. The other equivalents in the second determinant come from the relations $du = Tds - pdv$ and $d\mu = -sdT + vdp$ and the definitions $s = S/m$, $v = V/m$ and $u = U/m$. As a consequence we have only 5 derivatives which must be measured: $\partial s/\partial T$, $\partial v/\partial T$, $\partial v/\partial p$, s and v, while two of the Maxwellian relations reduce to identities. This somewhat surprising reduction of two relations to identities must be ascribed to the rather special definition of μ rather than to the general behavior of restricted systems.

In contrast to the above simple situation, if we choose as the x-set (T, V, m), J'_o becomes more involved.
Thus

(8)

$$J'_o = \frac{\partial(S, p, -\mu)}{\partial(T, V, m)} = \begin{vmatrix} \frac{\partial S}{\partial T} & \frac{\partial p}{\partial T} & \frac{-\partial \mu}{\partial T} \\ \frac{\partial S}{\partial V} & \frac{\partial p}{\partial V} & \frac{-\partial \mu}{\partial V} \\ \frac{\partial S}{\partial m} & \frac{\partial p}{\partial m} & \frac{-\partial \mu}{\partial m} \end{vmatrix} = \begin{vmatrix} \frac{m\partial s}{\partial T}, & \frac{\partial p}{\partial T}, & \left[s - v\left(\frac{\partial s}{\partial v}\right) \right] \\ \frac{\partial s}{\partial v}, & \frac{1}{m}\left(\frac{\partial p}{\partial v}\right), & \frac{-v}{m}\left(\frac{\partial p}{\partial v}\right) \\ \left[s - v\left(\frac{\partial s}{\partial v}\right) \right], & \frac{-v}{m}\left(\frac{\partial p}{\partial v}\right), & \frac{v^2}{m}\left(\frac{\partial p}{\partial v}\right) \end{vmatrix}$$

where in the second determinant the variable set has been changed from (T, V, m) to (T, v, m). This is readily done by the Jacobian method as an example will show. Thus take $(\partial S/\partial m)_{TV}$.

$$\left(\frac{\partial S}{\partial m}\right)_{TV} = \frac{\dfrac{\partial(S, V)}{\partial(m, v)_T}}{\dfrac{\partial(m, V)}{\partial(m, v)_T}} = \frac{\dfrac{\partial(ms, mv)}{\partial(m, v)_T}}{\dfrac{\partial(m, mv)}{\partial(m, v)_T}} = s - v\left(\frac{\partial s}{\partial v}\right)_T,$$

We notice that, although no element of this new modified Jacobian vanishes we still require only *five* partial derivatives (since s and v are really $(\partial S/\partial m)_{Tp}$ and $(\partial V/\partial m)_{Tp}$ respectively) and have only one significant Maxwellian relation. This illustrates the fact that although care in the selection of the x-set may reduce the complexity of results, it cannot reduce the actual number of physical parameters which must be determined experimentally.

4. Multicomponent Chemical Systems.

In chemical systems with more than one chemical component in equilibrium we have restricted systems having interesting variations of the properties discussed above. Now while this discussion does not produce any new results or results not deducible by conventional means, it does offer them in a compact and easily deduced form which is notably lacking in the usual presentation.[2] The Jacobian methods are further very flexible and enable changes of variable to be made so as to minimize intermediate steps and the consequent likelihood of error.

In a system of c chemical components (where c is by definition the number of chemical species whose masses can be varied independently), the c chemical potentials $\mu_1, \mu_2, \ldots \mu_c$ are always *restricted* variables. Depending on the number of phases present, other variables such as p or even T become restricted and the selection of the particular x-set which will be of greatest service in a particular case becomes of importance. We must therefore examine the situation in detail even at the expense of repeating much that is familiar to the chemical reader.

In the first place we must distinguish very clearly between n_i, the number of *intensity* variables which are independent, and n, the total number of independent variables of all sorts. Here $n_i \leqslant n$ and, for chemical systems under no other external force variable than pressure, is given by Gibbs' phase rule

$$n_i = c - \phi + 2$$

(where c is the number of chemical components and ϕ the number of distinct physical phases present).

[2] See for example R. W. Goranson, "Thermodynamic Relations in Multicomponent Systems," Carnegie Institute of Washington, D. C., 1930.

Useful as this rule is it does not fix n nor does it give us help in selecting x-sets in which less than the maximum number of intensity variables is utilized. In the case of the one component single phase system discussed in Sec. 3 we clearly have $n = 3$ and $n_i = 2$. The first x-set, (T,p,m), included the maximum number of intensity variables (2) and one extensive variable (m). In the second x-set, (T,V,m), one intensity and two extensive variables appear. But what happens when we go to a two-phase system? The value of n_i obviously decreases to unity, but does n remain the same? And what happens when we have two or more components?

5. Variables and Constraints in Chemical Systems.

From a somewhat superficial standpoint one might argue that a discussion of this sort is tautological. For in Eqn (2) of Sec. 1 if we set $l = c$, the number of independently variable masses, and consider T and p as two extra variables, then clearly $n = l + 2$, since it was explicitly stated that the number of terms in Eqns (1) and (2) was supposedly reduced to n, the number of independent variables required! But if this is so, what happens when p becomes a restricted variable? Does the number of terms in Eqns (1) and (2) depend on the number of phases present or not? Clearly we must consider the question of restrictions on the *masses* of the chemical species in our system as well as the method of determining the *value* of c in a given case.

We may regard the question of mass restrictions on a specific collection of chemicals under two headings: (a) variable total mass, and (b) constant total mass. The second case can further be broken up into (b_1) *constant mass systems* with semipermeable walls and so arranged that on withdrawing any one species we compensate by adding equivalent masses of one or more other species, and (b_2) *isolated systems* where the mass is constant because the walls are unpermeable to all chemical species. If we examine the definition of the number of components, c, naively, we might be tempted to say that if, in the case of a given set of non-reacting substances, the value were c for case (a) it would by definition be c-1 for case (b_1) and zero for case (b_2), since here we have no direct way of varying *any* mass at all.

It appears, however, that Gibbs regarded c as being fixed once for all as the *maximum number* of variable masses in the system. It is thus the maximum of potentially variable masses whatever later mass restrictions are imposed. This is clear from Gibbs' original discussion of the relation $n_i = c - \phi + 2$.[3] He repeatedly states that $c - \phi + 2$ gives the greatest conceivable number of *variations* in *phase* of which the system is capable. That is to say that $n_i = \phi_{max} - \phi$, and the system can vary from 1 through 2, 3, etc., up to ϕ_{max} phases, where this is given (when $n_i = 0$), by $\phi_{max} = c + 2$, and this value can be reached for a system without any reference to mass restrictions at all.

The determination of the value of c in many complicated systems is a difficult problem, though in the majority of cases met in practice rather readily settled. In the case of a collection of $\mathfrak{s}$ different stable and mutually inactive substances, $c \equiv \mathfrak{s}$. In the case of systems with one or more chemical reactions present we may extend our name chemical *substance* to include any chemical species (molecule or fragment) present in the system. If we then have a number, n_r, of independent equations connecting these species (and these may include reactions of all sorts, ionizations, statements of electrical neutrality, etc.) we have $c = \mathfrak{s} - n_r$. Just which particular molecule or fragment to choose as a component in a given case is a matter of taste and experience. Once a given species has been selected as a component one caution is necessary regarding computing its total mass and concentration in a given phase. Thus if in a gaseous system we take H_2 as a component and the element existed at the same time as H and H_2O vapor, we should have to add the total equivalent in both these forms to the free molecular H_2 to get the total mass (and later, mass concentration) of this component.

With this in mind we may conveniently treat the system as though it were made up of $c = \mathfrak{s} - n_r$ non-reacting stable chemical substances.

6. Degrees of Freedom of a Chemical System.

Although Gibbs' phase rule is invaluable in all such discussions we must find n itself as well. The process will incidentally indi-

[3] J. W. Gibbs, Scientific Papers, Vol. I, page 76, *et seq.* (Longmans, Green and Company, 1906).

cate the subsidiary equations which must be used in all thermodynamic calculations as well as facilitate the selection of possible x-sets when these are not to be entirely primaries.

The general procedure is simply to list the number of variables, n_{var}, which we need for the description of systems of c components and ϕ phases. We then write down all the simultaneous and independent equations involving these variables. These will include arbitrary definitions and external constraints, as well as experimental laws. Since we need only the total number, n_{eq}, of these equations and, in the case of the laws of nature, their general functional form, this listing can be done in a very general way. Then the number of degrees of freedom, n, of the system is simply $n = n_{var} - n_{eq}$.

The variables may conveniently be divided into the extensive variables (masses and volumes) and the intensive variables (concentrations, pressures and all quantities which are functions of these alone). A collection of variables suitable for a c-component, ϕ-phase system is given in Table I below. Here subscripts refer to components and primes to phases. Thus m_2''', c_2''', and μ_2''' refer to the mass, mass concentration and chemical potential, respectively, of the *second* component in the *third* phase. When no prime occurs the property is that of the subscript *component*, where no subscript is present to that of the whole *phase*, and when neither is present to a property of the whole *system*. In the third column of the table is given the total number of variables of the group in question.

Table I

Group	*Variables*	*Number*
I (Extensive)	$m_1', m_2', \ldots m_c', m', V'$	$(c + 2)(\phi + 1)$
	$m_1'', m_2'', \ldots m_c'', m'', V''$	
	, , , , ,	
	, , , , ,	
	, , , , ,	
	$m_1^{\phi}, m_2^{\phi}, \ldots m_c^{\phi}, m^{\phi}, V^{\phi}$	
	$m_1, m_2, \ldots m_c, m, V$	
II (Intensive)	$c_1', c_2', \ldots c_c', T, p$	
	$c_1'', c_2'', \ldots c_c''$	
	, , ,	$(c\,\phi + 2)$
	, , ,	
	, , ,	
	$c_1^{\phi}, c_2^{\phi}, \ldots c_c^{\phi}$	
III (Intensive)	$\mu_1', \mu_2', \ldots \mu_c'$	
	, , ,	
	, , ,	$c\,\phi$
	, , ,	
	$\mu_1^{\phi}, \mu_2^{\phi}, \ldots \mu_c^{\phi}$	
	Total	$3\,\phi c + 2\phi + c + 4$

Adding the quantities in the right column gives us

$$n_{var} = 3\phi c + 2\phi + c + 4$$

as the total number of variables with which we are concerned.

Table II

Group	*Equations*	*Number*	
Mass and volume sums	$\sum_i m_i^j = m^j \quad (j = 1, 2, \dots \phi)$	ϕ	(9)
	$\sum_j m_i^j = m_i \quad (i = 1, 2, \dots c)$	c	
	$\sum_j \sum_i m_i^j = m, \quad \sum_j V^j = V$	2	
Equations of state	$V^j = V^j\,(T, p, m_1^j, \dots m_c^j), \quad (j = 1, \dots \phi)$	ϕ	(10)
Definitions of c's	$c_i^j = m_i^j / m^j, \ (i, j)$	ϕc	
Nature of μ's	$\mu_i^j = \mu_i^j\,(T, p, c_1^j, \dots c_c^j), \quad (i, j)$	ϕc	(11)
Gibbs' Criterion of Equilibrium	$\mu_i^1 = \mu_i^2 = \dots = \mu_i^\phi, \ (i = 1, \dots c)$	$c(\phi - 1)$	
	Total	$3\phi c + 2\phi + 2$	

In the same way in Table II are listed the independent equations connecting these variables, with the number of each type in the third column. The sum total of these gives us $n_{eq} = 3\phi c + 2\phi + 2$. Consequently[4] we have for n

$$n = n_{var} - n_{eq} = c + 2 \tag{12}$$

and the value of n is independent of the number of phases present.

We are therefore justified in rewriting Eqn (2) as a generalized form of Eqn (5) with $l = c$ terms of the form $\mu_i dm_i$, i.e.,

$$dU = TdS - pdV + \sum_{i=1}^{c} \mu_i \, dm_i \tag{13}$$

with the knowledge that n and hence the number of terms is independent of whether we have a single phase or the maximum number, $\phi_{max} = n = c + 2$.

On combining the phase rule with Eqn (12) we have

$$n = c + 2 = n_i + \phi$$

or

$$n = n_{(intensive)} + \phi_{(extensive)} \tag{14}$$

[4] If any component is missing from a phase then that concentration and mass drop out of n_{var} while one equation each drops out of the last two groups of Table II. Consequently this difference remains constant.

which simply means that if we employ the maximum number of intensive variables we shall then need in addition a number of extensive ones equal to the number of phases present.

Since the above discussion assumed the total mass variable we now add the case (b) situation with m = constant and have

$$\left.\begin{array}{l}\text{case (a) } n_a = n_i + \phi \\ \text{case (b) } n_b = n_i + (\phi - 1)\end{array}\right\} n_i = c + 2 - \phi \qquad (15)$$

as the general relations we sought. It is thus possible to take an x-set suitable for a case (a) system and by dropping out a suitable extensive variable (say m or V) have a suitable x-set for case (b).

As soon as we pass to systems with two phases or more, primary x-sets cease to be as useful as those involving certain of the subsidiary variables from Table II.

7. Relations in Single Phase Systems.

Although Eqn (13) is of the same form whatever the number of phases, due to the different choices of variables (and the consequent differences in subsidiary equations such as those in Table II and others) it is convenient to consider systems of single, double, and more, phases separately.

To begin with let us write down J'_o from Eqn (13) with primary x-set $(T, p, m_1, m_2, \ldots m_c)$. We have, with $\mu_1 dm_1$ as the key term:

$$J'_o = \frac{\partial(-S, V, \mu_1, \mu_2, \ldots \mu_c)}{\partial(T, p, m_1, m_2, \ldots m_c)} = \begin{vmatrix} \frac{-\partial S}{\partial T} & \frac{\partial V}{\partial T} & \frac{\partial \mu_1}{\partial T} & \frac{\partial \mu_2}{\partial T} & \cdots & \frac{\partial \mu_c}{\partial T} \\ \frac{-\partial S}{\partial p} & \frac{\partial V}{\partial p} & \frac{\partial \mu_1}{\partial p} & \frac{\partial \mu_2}{\partial p} & \cdots & \frac{\partial \mu_c}{\partial p} \\ \frac{-\partial S}{\partial m_1} & \frac{\partial V}{\partial m_1} & \frac{\partial \mu_1}{\partial m_1} & \frac{\partial \mu_2}{\partial m_1} & \cdots & \frac{\partial \mu_c}{\partial m_1} \\ \frac{-\partial S}{\partial m_2} & \frac{\partial V}{\partial m_2} & \frac{\partial \mu_1}{\partial m_2} & \frac{\partial \mu_2}{\partial m_2} & \cdots & \frac{\partial \mu_c}{\partial m_2} \\ , & , & , & , & & , \\ , & , & , & , & & , \\ , & , & , & , & & , \\ \frac{-\partial S}{\partial m_c} & \frac{\partial V}{\partial m_c} & \frac{\partial \mu_1}{\partial m_c} & \frac{\partial \mu_2}{\partial m_c} & \cdots & \frac{\partial \mu_c}{\partial m_c} \end{vmatrix} \qquad (16)$$

a square array of $(c + 2)^2$ terms with something less than $(c + 2)(c + 3)/2$ independent. The $(c + 2)(c + 1)/2$ Maxwellian relations are read off at once by inspection. In cases where we want a few of the Maxwellian relations without the bother of writing out the square array we may do so from the differential symbol of J'_o itself. Thus the main diagonal elements are given by forming the derivative of a Y-variable with the x immediately below it (such as $-\partial S/\partial T$, $\partial V/\partial p$, etc.). All the others are connected in pairs, where any desired pair is obtained by simply selecting the desired Y's together with the x's below them and equating the "cross" differentials. Thus let $(-S, \mu_1)$ be the desired Y's. We write the scheme: $\begin{matrix} -S \\ T \end{matrix} \times \begin{matrix} \mu_1 \\ m_1 \end{matrix}$ and the wanted relation is simply $-(\partial S/\partial m_1)_{Tp\ldots} = (\partial \mu_1/\partial T)_{pm_1\ldots}$.

Again with V and μ_6 we have at once the array $\begin{matrix} V \\ p \end{matrix} \times \begin{matrix} \mu_6 \\ m_6 \end{matrix}$ and so

$$(\partial V/\partial m_6)_{Tp,m_1\ldots} = (\partial \mu_6/\partial p)_{Tm_1\ldots}, \text{ etc.}$$

The procedure is satisfactory as long as the Y's are taken with their proper signs, whatever their relative position in the differential symbol for J'_o may be.

Another set of variables may be used in which the maximum permitted number of intensity variables, $c + 1$, and a *single* extensive variable are employed. For this set we take $(T,p,c_1,c_2,\ldots c_{c-1},m)$ and eliminate the component masses $m_1,m_2,\ldots m_c$ from Eqn (13). Using the defining equations for the c's from Table II together with $m = \sum_i m_i$ and $\sum_i c_i = 1$ we have, after regrouping terms,

$$dU = TdS - pdV + m(\mu_1 - \mu_2)dc_1 + m(\mu_2 - \mu_1)dc_2 + \ldots + m(\mu_{c-1} - \mu_c)dc_{c-1} + \left[(\mu_1 - \mu_c)c_1 + (\mu_2 - \mu_c)c_2 + \ldots + (\mu_{c-1} - \mu_c)\,c_{c-1} + \mu_c\right]dm \tag{17}$$

or

$$d\dot{U} = Tds - pdV + B_1 dc_1 + B_2 dc_2 + \ldots + B_{c-1}\, dc_{c-1} + B_c dm \tag{18}$$

where the B's are simply abbreviations for the coefficients of Eqn (17). We notice in particular that

$$\begin{aligned} B_i &= B_i(T,p,c_1,c_2 \ldots c_{c-1},m) \qquad i<c \\ B_c &= B_c(T,p,c,c_2 \ldots c_{c-1}) \end{aligned}$$

which therefore makes B_c a restricted variable since it is independent of m.

We may now write out the new modified Jacobian in terms of this new x-set, where since B_c is a restricted variable a zero occurs in the lower right-hand corner. We notice further that since $\partial B_1/\partial m = B_1/m$ and by symmetry $\partial B_1/\partial m = \partial B_c/\partial c_1$, the latter derivative is simply B_1/m, etc., with $\partial B_c/\partial m = 0$ as the last element of the column. As a result the new Jacobian has a single zero on the main diagonal and $(c\text{-}1)$ derivatives above this, which do not need to be measured as derivatives.

$$J'_o = \frac{\partial(-S,V,B_1,B_2 \ldots B_{c-1},B_c)}{\partial(T,p,c_1,c_2,\ldots c_{c-1},m)} = \begin{vmatrix} \frac{-\partial S}{\partial T} & \frac{\partial V}{\partial T} & \frac{\partial B_1}{\partial T} & \frac{\partial B_2}{\partial T} & \cdots & \frac{\partial B_{c-1}}{\partial T} & \frac{\partial B_c}{\partial T} \\ \frac{-\partial S}{\partial p} & \frac{\partial V}{\partial p} & \frac{\partial B_1}{\partial p} & \frac{\partial B_2}{\partial p} & \cdots & \frac{\partial B_{c-1}}{\partial p} & \frac{\partial B_c}{\partial p} \\ \frac{-\partial S}{\partial c_1} & \frac{\partial V}{\partial c_1} & \frac{\partial B_1}{\partial c_1} & \frac{\partial B_2}{\partial c_1} & \cdots & \frac{\partial B_{c-1}}{\partial c_1} & \frac{B_1}{m} \\ \frac{-\partial S}{\partial c_2} & \frac{\partial V}{\partial c_2} & \frac{\partial B_1}{\partial c_2} & \frac{\partial B_2}{\partial c_2} & \cdots & \frac{\partial B_{c-1}}{\partial c_2} & \frac{B_2}{m} \\ , & , & , & , & & , & , \\ , & , & , & , & & , & , \\ , & , & , & , & & , & , \\ \frac{-\partial S}{\partial c_{c-1}} & \frac{\partial V}{\partial c_{c-1}} & \frac{\partial B_1}{\partial c_{c-1}} & \frac{\partial B_2}{\partial c_{c-1}} & \cdots & \frac{\partial B_{c-1}}{\partial c_{c-1}} & \frac{B_{c-1}}{m} \\ \frac{-\partial S}{\partial m} & \frac{\partial V}{\partial m} & \frac{B_1}{m} & \frac{B_2}{m} & \cdots & \frac{B_{c-1}}{m} & 0 \end{vmatrix} \tag{19}$$

Although the Jacobians of Eqns (16) and (19) can now be used to calculate any desired thermodynamic property of the general chemical system, little information is gained which cannot more readily be got from specific examples. This is all the more true since in practice we seldom have more than two components and in such cases can readily use the appropriate part of the general results above.

8. Two Component Single Phase Systems.

If for purposes of illustrating the directness and flexibility of Jacobian methods we confine ourselves to systems of *two* components Eqn (13) reduces to four terms, since $n = 4$, and we have

$$dU = TdS - pdV + \mu_1 dm_1 + \mu_2 dm_2 \qquad (20)$$

and with the primary x-set (T,p,m_1,m_2) the modified Jacobian is a special case of that in Eqn (16). Hence

$$J'_o = \frac{\partial(-S,V,\mu_1,\mu_2)}{\partial(T,p,m_1,m_2)} = \begin{vmatrix} \frac{-\partial S}{\partial T} & \frac{\partial V}{\partial T} & \frac{\partial \mu_1}{\partial T} & \frac{\partial \mu_2}{\partial T} \\ \frac{-\partial S}{\partial p} & \frac{\partial V}{\partial p} & \frac{\partial \mu_1}{\partial p} & \frac{\partial \mu_2}{\partial p} \\ \frac{-\partial S}{\partial m_1} & \frac{\partial V}{\partial m_1} & \frac{\partial \mu_1}{\partial m_1} & \frac{\partial \mu_2}{\partial m_1} \\ \frac{-\partial S}{\partial m_2} & \frac{\partial V}{\partial m_2} & \frac{\partial \mu_1}{\partial m_2} & \frac{\partial \mu_2}{\partial m_2} \end{vmatrix} = \begin{vmatrix} -a_0 & a_1 & a_2 & a_3 \\ a_1 & a_{11} & a_{12} & a_{13} \\ a_2 & a_{12} & a_{22} & a_{23} \\ a_3 & a_{13} & a_{23} & a_{33} \end{vmatrix} \qquad (21)$$

Here the a's are simply convenient abbreviations for the derivatives which, due to the symmetry, are reduced from 16 to 10 independent ones. Each of the derivatives in turn represents some physical property of the system. Thus the top row gives temperature changes, the left column heat properties (essentially), etc. In particular a_0 is written with a minus sign since then $a_0 = (\partial S/\partial T)_{pm_1m_2}$ and $T(\partial S/\partial T)_{pm_1m_2} = C_{pm_1m_2}$, the heat capacity of the system at constant (p,m_1,m_2), usually a positive quantity. Of course many of the terms, in fact the four in the

upper left corner, can be written in other ways. Thus with

$$S = ms \text{ and } V = mv, \ (\partial S/\partial m)_{Tpm_2} =$$

$$s + m(\partial s/\partial m_1)_{Tpm_2}, \ (\partial V/\partial m_1)_{Tpm_2}$$

$$= v + (\partial v/\partial m)_{Tpm_2}, \text{ etc.}$$

To determine any property involving other x-sets in terms of the a's we proceed with the usual Jacobian transformation, to change from the new x-set to the old one, (T,p,m_1,m_2). If we take $C_{Vm_1m_2}$, the heat capacity at constant (V,m_1m_2), we must first notice that

$$C_{Vm_1m_2} = \frac{dQ_{Vm_1m_2}}{dT} = T\left(\frac{\partial S}{\partial T}\right)_{Vm_1m_2}$$

and we must essentially transform an entropy derivative in terms of the x-set (T,V,m_1,m_2) to the set (T,p,m_1,m_2). We have

$$\left(\frac{\partial S}{\partial T}\right)_{Vm_1m_2} = \frac{\partial(S,V,m_1,m_2)}{\partial(T,V,m_1,m_2)} = \frac{\dfrac{\partial(S,V,m_1,m_2)}{\partial(T,p,m_1,m_2)}}{\dfrac{\partial(T,V,m_1,m_2)}{\partial(T,p,m_1,m_2)}} = \frac{\dfrac{\partial(S,V)}{\partial(T,p)}_{m_1,m_2}}{\left(\dfrac{\partial V}{\partial p}\right)_{Tm_1m_2}}$$

where, as usual, variables written outside a bracket or a Jacobian are constant for all differentiations involved. We now need only read off the equivalents in the upper corner of the determinant of the a's in Eqn (21) to have

$$C_{Vm_1m_2} = T\frac{\begin{vmatrix} a_0 & a_1 \\ -a_1 & a_{11} \end{vmatrix}}{a_{11}} = \frac{T(a_0a_{11} + a_1^2)}{a_{11}}, \tag{22}$$

a result independent of the number of components.

Again, to obtain the heat of addition per formula mass of, say, component 1 at constant (T,V,m_2), we proceed as follows. If M_1

is the molecular " weight " of this component then $dm_1 = M_1 dv_1$, if dv is the change in the number of moles of 1 corresponding to a change of mass dm_1.

Thus $$\frac{dQ}{dm_1}_{TVm_2} = \frac{1}{M_1}\frac{dQ}{dv_1}_{TVm_2} = T\left(\frac{\partial S}{\partial m_1}\right)_{TVm_2}$$

and $$\left(\frac{\partial S}{\partial m_1}\right)_{TVm_2} = \frac{\partial(S,T,V,m_2)}{\partial(m_1,T,V,m_2)} = \frac{\dfrac{\partial(S,T,V,m_2)}{\partial(m_1,T,p,m_2)}}{\dfrac{\partial(m_1,T,V,m_2)}{\partial(m_1,T,p,m_2)}} =$$

$$\frac{\dfrac{\partial(S,V)}{\partial(m_1,p)}_{Tm_2}}{\left(\dfrac{\partial V}{\partial p}\right)_{Tm_1m_2}} = -\frac{\begin{vmatrix} -a_1 & a_{11} \\ -a_2 & a_{12} \end{vmatrix}}{a_{11}}$$

where the minus sign outside the numerator arises from interchanging the order of (m_1,p) to give correspondence with that employed in Eqn (21). This gives finally

$$\frac{dQ}{dv_1}_{TVm_2} = M_1 T \frac{(a_1a_{12} - a_2a_{11})}{a_{11}} \qquad (23)$$

The chemical potentials μ_1 and μ_2 are functions of intensity variables alone and hence, although depending directly on T and p, vary with m_1 and m_2 only as these alter the concentrations. As a result the present x-set does not reveal the true character of the derivatives of the type $(\partial\mu_1/\partial m_1)_{Tpm_2}$, $(\partial\mu_2/\partial m_1)_{Tpm_2}$, etc.

For this purpose the second x-set, (T,p,c,m), used in Eqn (19) is preferable and we accordingly express these derivatives in terms of it.[5] The first of these gives us

[5] In this section only the symbol c stands for c_1, the concentration of the *first* component, and is not to be confused with c, the number of components which is here two, and of course not a variable.

$$\left(\frac{\partial \mu_1}{\partial m_1}\right)_{m_2 Tp} = \frac{\partial(\mu_1,m_2,T,p)}{\partial(m_1,m_2,T,p)} = \frac{\dfrac{\partial(\mu_1,m_2,T,p)}{\partial(c,m,T,p)}}{\dfrac{\partial(m_1,m_2,T,p)}{\partial(c,m,T,p)}} = \frac{\dfrac{\partial(\mu_1,m_2)}{\partial(c,m)_{Tp}}}{\dfrac{\partial(m_1,m_2)}{\partial(c,m)_{Tp}}}$$

where the order of the new x-set has been written (c,m,T,p) simply to facilitate "cancellation" without any troublesome sign changes. With $m_1 = mc$ and $m_2 = m(1-c)$ this result reduces to

$$(\partial\mu_1/\partial m_1)_{Tpm_2} = \frac{(1-c)}{m}(\partial\mu_1/\partial c)_{Tpm}, \text{ and likewise}$$

$$(\partial\mu_2/\partial m_1)_{Tpm_2} = \frac{(1-c)}{m}(\partial\mu_2/\partial c)_{Tpm}$$

$$(\partial\mu_2/\partial m_2)_{Tpm_1} = \frac{-c}{m}(\partial\mu_2/\partial c)_{Tpm}$$

$$(\partial\mu_1/\partial m_2)_{Tpm_1} = \frac{-c}{m}(\partial\mu_1/\partial c)_{Tpm}$$

Then since the second and fourth of these are equal by symmetry we need measure only *one* derivative, say $(\partial\mu_1/\partial c)_{Tpm}$ (and not three). For this reason it is possible to deduce all the properties of this system from 8 rather than 10 fundamental derivatives say (a_0, a_1, a_2, a_3, a_{11}, a_{12}, a_{13}, and $(\partial\mu_1/\partial c)_{Tpm}$).

Another result is of interest. Since constant (m_1, m_2) and constant (c, m) are essentially equivalent as far as all derivatives in the two top rows of the Jacobian of Eqn (21) are concerned, all these derivatives are the same for the sets (T,p,m_1,m_2) and (T,p,c,m).

The above discussion suggests that we can with profit turn to the form of Eqn (18) corresponding to two components, viz.:

$$dU = TdS - pdV + B_1dc + B_2dm. \qquad (24)$$

Here the modified Jacobian is

(25)

$$J'_o = \frac{\partial(-S,V,B_1,B_2)}{\partial(T,p,c,m)} = \begin{vmatrix} \frac{-\partial S}{\partial T} & \frac{\partial V}{\partial T} & \frac{\partial B_1}{\partial T} & \frac{\partial B_2}{\partial T} \\ \frac{-\partial S}{\partial p} & \frac{\partial V}{\partial p} & \frac{\partial B_1}{\partial p} & \frac{\partial B_2}{\partial p} \\ \frac{-\partial S}{\partial c} & \frac{\partial V}{\partial c} & \frac{\partial B_1}{\partial c} & \frac{\partial B_2}{\partial c} \\ \frac{-\partial S}{\partial m} & \frac{\partial V}{\partial m} & \frac{\partial B_1}{\partial m} & \frac{\partial B_2}{\partial m} \end{vmatrix} = \begin{vmatrix} -b_0 & b_1 & b_2 & b_3 \\ b_1 & b_{11} & b_{12} & b_{13} \\ b_2 & b_{12} & b_{22} & \frac{B_1}{m} \\ b_3 & b_{13} & \frac{B_1}{m} & 0 \end{vmatrix}$$

Again examination shows that, as before, we need measure only 8 actual derivatives for all the quantities in the square arrays to be determined.

Since derivatives involving secondary quantities can be treated as readily as other derivatives, take the case of $(\partial U/\partial S)_{VTc}$ and let us express it in terms of the b's. As before

$$\left(\frac{\partial U}{\partial S}\right)_{VTc} = \frac{\partial(U,V,T,c)}{\partial(S,V,T,c)} = \frac{\dfrac{\partial(U,V,T,c)}{\partial(p,m,T,c)}}{\dfrac{\partial(S,V,T,c)}{\partial(p,m,T,c)}} = \frac{\dfrac{\partial(U,V)}{\partial(p,m)_{Tc}}}{\dfrac{\partial(S,V)}{\partial(p,m)_{Tc}}}$$

Here primary derivatives come directly from Eqn (25) while partials of U must be got from Eqn (24) and then replaced by their equivalent b's. The result is finally

$$\left(\frac{\partial U}{\partial S}\right)_{VTc} = \frac{\left(\dfrac{\partial U}{\partial p}\right)_{TCm} \cdot b_{13} - \left(\dfrac{\partial U}{\partial m}\right)_{Tcp} \cdot b_{11}}{-b_1 b_{13} + b_3 b_{11}} =$$

$$\frac{(Tb_1 + pb_{11})b_{13} + (Tb_3 + pb_{13} - B_2)b_{11}}{b_1 b_{13} - b_3 b_{11}}$$

The present set of variables is well suited to the special case of fixed mass, for in this case we simply drop the last term of Eqn (24) and suppress the bottom row and right column of J'_o, Eqn (25).

9. Two Components and Two Phases.

The chief differences when multiphase systems are encountered arise from the increase in the number of restrictions with the consequent alteration in the possible x-sets.

When we pass from one to two phases the set $(T,p,m_1,m_2,\ldots m_c)$ no longer is possible, since $p = p(T,c_1,c_2,\ldots c_{c-1})$. Since $n_i = c - \phi + 2 = c$ we must then omit either T or p (usually the latter) and introduce an extensive variable (often V). In the case of two components and (T,V,m_1,m_2) as the x-set we select $\mu_1 dm_1$ as the key term and have

$$J'_o = \frac{\partial(-S,-p,\mu_1,\mu_2)}{\partial(T,V,m_1,m_2)} = \begin{vmatrix} \frac{-\partial S}{\partial T} & \frac{-\partial p}{\partial T} & \frac{\partial \mu_1}{\partial T} & \frac{\partial \mu_2}{\partial T} \\ \frac{-\partial S}{\partial V} & \frac{-\partial p}{\partial V} & \frac{\partial \mu_1}{\partial V} & \frac{\partial \mu_2}{\partial V} \\ \frac{-\partial S}{\partial m_1} & \frac{-\partial p}{\partial m_1} & \frac{\partial \mu_1}{\partial m_1} & \frac{\partial \mu_2}{\partial m_1} \\ \frac{-\partial S}{\partial m_2} & \frac{-\partial p}{\partial m_2} & \frac{\partial \mu_1}{\partial m_2} & \frac{\partial \mu_2}{\partial m_2} \end{vmatrix} \qquad (26)$$

Now unfortunately although we can read Maxwell's relations directly out of Eqn (26), this set of variables is not as convenient experimentally as other sets made up chiefly of non-primary variables. A very convenient one for this purpose is (T,c'_1,m',m'') where c'_1 is the concentration of the first component in phase one and m' and m'' are the respective phase masses. For this change we need the following equations from Table II, as well as relations for S and V in terms of specific quantities.

$$\begin{array}{llll} m_1 = c'_1\, m' + c''_1\, m'' & c'_1 + c'_2 = 1 & S = m's' + m''s'' \\ m_2 = c'_2\, m' + c''_2\, m'' & c''_1 + c''_2 = 1 & V = m'v' + m''v'' \end{array}$$

Then we may readily determine any derivative in Eqn (26) directly in terms of our new variables.

Thus to express $\left(\frac{\partial S}{\partial T}\right)_{V m_1 m_2}$, for example, in terms of $(T,c''_1,m',m'',)$ we have

$$\left(\frac{\partial S}{\partial T}\right)_{Vm_1m_2} = \frac{\partial(S,V,m_1,m_2)}{\partial(T,V,m_1,m_2)} = \frac{\dfrac{\partial(S,V,m_1,m_2)}{\partial(T,c_1',m',m'')}}{\dfrac{\partial(T,V,m_1,m_2)}{\partial(T,c_1',m',m'')}} = \frac{J^{SV}}{J_{11}^{SV}}$$

where J^{SV} is simply an abbreviation for the fourth order Jacobian in the numerator and J_{11}^{SV} represents the third order Jacobian resulting from suppressing the *first* row and *first* column of J^{SV}. We now write out J^{SV}

$$J^{SV} = \begin{vmatrix} \dfrac{\partial S}{\partial T} & \dfrac{\partial V}{\partial T} & \dfrac{\partial m_1}{\partial T} & \dfrac{\partial m_2}{\partial T} \\ \dfrac{\partial S}{\partial c_1'} & \dfrac{\partial V}{\partial c_1'} & \dfrac{\partial m_1}{\partial c_1'} & \dfrac{\partial m_2}{\partial c_1'} \\ \dfrac{\partial S}{\partial m'} & \dfrac{\partial V}{\partial m'} & \dfrac{\partial m_1}{\partial m'} & \dfrac{\partial m_2}{\partial m'} \\ \dfrac{\partial S}{\partial m''} & \dfrac{\partial V}{\partial m''} & \dfrac{\partial m_1}{\partial m''} & \dfrac{\partial m_2}{\partial m''} \end{vmatrix} = \begin{vmatrix} d_1 & d_2 & d_3 & d_4 \\ d_5 & d_6 & d_7 & d_8 \\ s' & v' & c_1' & c_2' \\ s'' & v'' & c_1'' & c_2'' \end{vmatrix} \qquad (27)$$

where d_1, d_2, etc., can be expressed in terms of masses and specific variables if desired.

(Thus $d_1 = m'\dfrac{\partial s'}{\partial T} + m''\dfrac{\partial s''}{\partial T}$, $d_4 = -d_3$, $d_8 = -d_7$, etc.)

In the same way the other elements of the first column of the array in Eqn (26) can now be found.

Thus $$\left(\frac{\partial S}{\partial V}\right)_{m_1m_2T} = \frac{\dfrac{\partial(S,m_1,m_2)}{\partial(c_1',m',m'')_T}}{\dfrac{\partial(V,m_1,m_2)}{\partial(c_1',m',m'')_T}} = \frac{J_{12}^{SV}}{J_{11}^{SV}}$$

$$\left(\frac{\partial S}{\partial m_2}\right)_{Vm_1T} = \frac{\dfrac{\partial(S,V,m_1)}{\partial(c_1',m',m'')_T}}{\dfrac{\partial(m_2,V,m_1)}{\partial(c_1',m',m'',)_T}} = \frac{J_{14}^{SV}}{\dfrac{\partial(V,m_1,m_2)}{\partial(c_1',m',m'')_T}} = \frac{J_{14}^{SV}}{J_{11}^{SV}}$$

The elements of the second, third, and fourth rows of the Jacobian of Eqn (26) need Jacobians which we shall designate as J^{pV}, $J^{\mu_1 V}$ and $J^{\mu_2 V}$ respectively. Writing these out we have

$$J^{pV} \equiv \frac{\partial(p,V,m_1,m_2)}{\partial(T,c_1',m',m'')} = \begin{vmatrix} \frac{\partial p}{\partial T} & \frac{\partial V}{\partial T} & \frac{\partial m_1}{\partial T} & \frac{\partial m_2}{\partial T} \\ \frac{\partial p}{\partial c_1'} & \frac{\partial V}{\partial c_1'} & \frac{\partial m_1}{\partial c_1'} & \frac{\partial m_2}{\partial c_1'} \\ \frac{\partial p}{\partial m'} & \frac{\partial V}{\partial m'} & \frac{\partial m_1}{\partial m'} & \frac{\partial m_2}{\partial m'} \\ \frac{\partial p}{\partial m''} & \frac{\partial V}{\partial m''} & \frac{\partial m_1}{\partial m''} & \frac{\partial m_2}{\partial m''} \end{vmatrix} = \begin{vmatrix} d_9 & d_2 & d_3 & d_4 \\ d_{10} & d_6 & d_7 & d_8 \\ 0 & v' & c_1' & c_2' \\ 0 & v'' & c_1'' & c_2'' \end{vmatrix} \tag{28}$$

(29)

$$J^{\mu_1 V} \equiv \frac{\partial(\mu_1,V,m_1,m_2)}{\partial(T,c_1',m',m'')} = \begin{vmatrix} \frac{\partial \mu_1}{\partial T} & \frac{\partial V}{\partial T} & \frac{\partial m_1}{\partial T} & \frac{\partial m_2}{\partial T} \\ \frac{\partial \mu_1}{\partial c_1'} & \cdot & \cdot & \cdot \\ \frac{\partial \mu_1}{\partial m'} & \cdot & \cdot & \cdot \\ \frac{\partial \mu_1}{\partial m''} & \cdot & \cdot & \cdot \end{vmatrix} = \begin{vmatrix} d_{11} & d_2 & d_3 & d_4 \\ d_{12} & d_6 & d_7 & d_8 \\ 0 & v' & c_1' & c_2' \\ 0 & v'' & c_1'' & c_2'' \end{vmatrix}$$

and

(30)

$$J^{\mu_2 V} \equiv \frac{\partial(\mu_2,V,m_1,m_2)}{\partial(T,c_1',m',m'')} = \begin{vmatrix} \frac{\partial \mu_2}{\partial T} & \frac{\partial V}{\partial T} & \frac{\partial m_1}{\partial T} & \frac{\partial m_2}{\partial T} \\ \frac{\partial \mu_2}{\partial c_1'} & \cdot & \cdot & \cdot \\ \frac{\partial \mu_2}{\partial m'} & \cdot & \cdot & \cdot \\ \frac{\partial \mu_2}{\partial m''} & \cdot & \cdot & \cdot \end{vmatrix} = \begin{vmatrix} d_{13} & d_2 & d_3 & d_4 \\ d_{14} & d_6 & d_7 & d_8 \\ 0 & v' & c_1' & c_2' \\ 0 & v'' & c_1'' & c_2'' \end{vmatrix}$$

They are seen to differ among themselves and from J^{SV} only in the first column. Hence J_{11} is the same, whichever of the four Eqns., (27) to (30), we use. Thus

$$\left(\frac{\partial p}{\partial V}\right)_{Tm_1m_2} = \frac{\dfrac{\partial(p,m_1,m_2)}{\partial(c_1',m',m'')_T}}{\dfrac{\partial(V,m_1,m_2)}{\partial(c_1',m',m'')_T}} = \frac{J_{12}^{pV}}{J_{11}} = \frac{d_{10}(c_1'c_2'' - c_1''c_2')}{J_{11}}$$

$$\left(\frac{\partial p}{\partial m_1}\right)_{TVm_2} = \frac{\dfrac{\partial(p,V,m_2)}{\partial(c_1',m',m'')_T}}{\dfrac{\partial(m_1,V,m_2)}{\partial(c_1',m',m'')_T}} = \frac{J_{13}^{pV}}{-J_{11}} = \frac{d_{10}(v'c_2'' - v''c_2')}{-J_{11}}$$

$$\left(\frac{\partial \mu_1}{\partial m_1}\right)_{TVm_2} = \frac{\dfrac{\partial(\mu_1,V,m_2)}{\partial(c_1',m',m'')_T}}{\dfrac{\partial(m_1,V,m_2)}{\partial(c_1',m',m'')_T}} = \frac{J_{13}^{\mu_1 V}}{-J_{11}} = \frac{d_{12}(v'c_2'' - v''c_2')}{-J_{11}}$$

$$\left(\frac{\partial \mu_2}{\partial T}\right)_{Vm_1m_2} = \frac{J^{\mu_2 V}}{J_{11}}, \quad \left(\frac{\partial \mu_2}{\partial m_2}\right)_{TVm_1} = \frac{J_{14}^{\mu_2 V}}{J_{11}}, \text{ etc.}$$

Other useful sets such as (T, c_1', x m) may be used where $x = m''/m$, the mass ratio in the second phase. Since this offers no special divergencies from the usual technique, no example need be worked out.

10. Two Components and Three Phases.

When another phase is added to our system, $n_i = c - 3 + 2 = 1$. Thus only one intensity variable is allowed and this we shall take as T. This gives the same variable set as used in Eqn (26), i.e., (T,V,m_1,m_2), but here we have more rigorously restricted dependent variables. Thus $p = p(T)$,$\mu_1 = \mu_1(T)$,$\mu_2 = \mu_2(T)$ and our modified Jacobian becomes much simpler.

(31)

$$J'_o = \frac{\partial(-S,-p,\mu_1\,\mu_2)}{\partial(T,V,m_1,m_2)} = \begin{vmatrix} \frac{-\partial S}{\partial T} & \frac{-\partial p}{\partial T} & \frac{\partial \mu_1}{\partial T} & \frac{\partial \mu_2}{\partial T} \\ \frac{-\partial S}{\partial V} & \frac{-\partial p}{\partial V} & \frac{\partial \mu_1}{\partial V} & \frac{\partial \mu_2}{\partial V} \\ \frac{-\partial S}{\partial m_1} & \frac{-\partial p}{\partial m_1} & \frac{\partial \mu_1}{\partial m_1} & \frac{\partial \mu_2}{\partial m_1} \\ \frac{-\partial S}{\partial m_2} & \frac{-\partial p}{\partial m_2} & \frac{\partial \mu_1}{\partial m_2} & \frac{\partial \mu_2}{\partial m_2} \end{vmatrix} = \begin{vmatrix} \frac{-\partial S}{\partial T} & \frac{dp}{\partial T} & \frac{d\mu_1}{\partial T} & \frac{d\mu_1}{\partial T} \\ \frac{-\partial S}{\partial V} & 0 & 0 & 0 \\ \frac{-\partial S}{\partial m_1} & 0 & 0 & 0 \\ \frac{-\partial S}{\partial m_2} & 0 & 0 & 0 \end{vmatrix}$$

Here we have 3 independent Maxwell relations and thus only 4 independent derivatives in terms of which all other properties can be computed.

As before, a more practical experimental x-set is given by (T, m', m'', m''). Any of the derivatives in the first column of Eqn (31) can be got as ratios readily expressed in terms of a Jacobian of $(S,V,m_1\,m_2)$ with respect to this new set. Thus

$$\left(\frac{\partial S}{\partial T}\right)_{Vm_1m_2} = \frac{\frac{\partial(S,V,m_1\,m_2)}{\partial(T,m',m'',m''')}}{\frac{\partial(T,V,m_1,m_2)}{\partial(T,m',m'',m''')}} = \frac{J_{00}}{J_{11}}$$

where J_{11} is the minor of J_{00} obtained by suppressing the first row and column as before.

Writing J_{00} out for reference gives

$$J_{00} = \begin{vmatrix} \frac{\partial S}{\partial T} & \frac{\partial V}{\partial T} & \frac{\partial m_1}{\partial T} & \frac{\partial m_2}{\partial T} \\ \frac{\partial S}{\partial m'} & \frac{\partial V}{\partial m'} & \frac{\partial m_1}{\partial m'} & \frac{\partial m_2}{\partial m'} \\ \frac{\partial S}{\partial m''} & \frac{\partial V}{\partial m''} & \frac{\partial m_1}{\partial m''} & \frac{\partial m_2}{\partial m''} \\ \frac{\partial S}{\partial m'''} & \frac{\partial V}{\partial m'''} & \frac{\partial m_1}{\partial m'''} & \frac{\partial m_2}{\partial m'''} \end{vmatrix} = \begin{vmatrix} e_1 & e_2 & e_3 & e_4 \\ s' & v' & c'_1 & c'_2 \\ s'' & v'' & c''_1 & c''_2 \\ s''' & v''' & c'''_1 & c'''_2 \end{vmatrix} \quad (32)$$

Here c_1', c_2'' and c_3''' are included for symmetry even though $c_1' + c_2' = 1$, etc., for the other two pairs. Further, the e's are abbreviations for sums over the three phases, i.e.,

$$e_1 = \sum m^i \frac{ds_i}{dT}, \quad e_2 = \sum m^i \frac{dv^i}{dT}, \quad e_3 = \sum m_1^i \frac{dc_1^i}{dT} \text{ and}$$

$$e_4 = -\sum m_2^i \frac{dc_1^i}{dT}.$$

Here of course the s's, v's and c's are all functions of T only. Using the Jacobian J_{00} we can obtain the other S derivatives:

$$\left(\frac{\partial S}{\partial V}\right)_{Tm_1m_2} = \frac{\dfrac{\partial(S,m_1,m_2)}{\partial(m',m'',m''')_T}}{\dfrac{\partial(V,m_1,m_2)}{\partial(m',m'',m''')_T}} = \frac{J_{12}}{J_{11}}$$

$$\left(\frac{\partial S}{\partial m_1}\right)_{TVm_2} = \frac{\dfrac{\partial(S,V,m_2)}{\partial(m',m'',m''')_T}}{\dfrac{\partial(m_1\, V\, m_2)}{\partial(m',m'',m''')_T}} = \frac{J_{13}}{-J_{11}}, \quad \left(\frac{\partial S}{\partial m_2}\right)_{TVm_1} = \frac{J_{14}}{J_{11}}.$$

The same Jacobian J_{00} is also of use for changing from, say, the x-set (T,V,m',m'') to (T,m',m'',m'''). Thus

$$\left(\frac{\partial S}{\partial T}\right)_{Vm'm''} = \frac{\dfrac{\partial(S,V,m',m'')}{\partial(T,m',m'',m''')}}{\dfrac{\partial(T,V,m',m'')}{\partial(T,m',m'',m''')}} = \frac{\dfrac{\partial(S,V)}{\partial(T,m''')}_{m'm''}}{\dfrac{\partial(V)}{\partial(m''')}_{m'm''T}} = \frac{\begin{vmatrix} e_1 & e_2 \\ s''' & v''' \end{vmatrix}}{v'''}$$

with similar results when we start with (T,V,m',m''') or (T,V,m'',m''').

Other choices such as (T, x', x'', m), where x' and x'' are the mass fractions in the first and second phases respectively, may be similarly treated.

We note finally that on suppressing the bottom row and right column of the array in Eqn (31) we have the appropriate results for the *two* phase *single* component system.

In the case of two component systems with four phases we have invariancy, and T, μ_1, μ_2 and all specific entropies and volumes are constant. Thus the only variables in Eqn (13) are S, V, m_1 and m_2, and these can be altered only through changing the masses of one or more phases. Consequently any desired quantities can be got more or less by inspection and although interesting transformative Jacobians can be set up, their use is rather artificial.

It is hoped that the above treatment will serve to show the great directness and power of the Jacobian method of treating the thermodynamic properties of chemical systems. The results, further, involve a minimum of intermediate steps and auxiliary equations and, left in determinant form, are as compact and easy to handle as the complexity of the situation permits.

F. H. CRAWFORD
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Málaga, Spain

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